REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

1. REPORT DATE (DD-MM-YYYY) 28-07-2003	2. REPORT TYPE final technical report	3. DATES COVERED (From - To) 15 January 2003 to 28 July 2003

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Improved Daily Nitrate and Ammonium Concentration Models for the Chesapeake Bay Watershed FINAL REPORT	DACW42-03-P-0236
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Lynch, James, A	
Grimm, Jeffrey, W	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
James A. Lynch, Consultant Dr. James A. Lynch 1401 E. Park Hills Avenue State College, PA 16803-3246	

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
United States Army Corps of Engineers, USAERDC, Attn: Carl Cerco, Waterways 3909, Halls Ferry Road, Vicksburg, MS 39180-6199 and United States Environmental Protection Agency, Chesapeake Bay Watershed Program Chesapeake Bay Program Office 410 Severn Avenue, Annapolis, MD 21403	US ACE, US EPA
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

no limitations on distribution/availability

13. SUPPLEMENTARY NOTES

20030806 123

14. ABSTRACT

A revised model of daily ammonium and nitrate wet-fall concentration and wet deposition was developed for use in the Phase 5 Chesapeake Bay Watershed Modeling Program. The preceding model (Valigura et al, 1996) was based on precipitation chemistry data from 1984 through 1992. The revised model was derived data from 1984 through 2001 and was extended to include parameters of precipitation event history, land cover composition, and long-term concentration trends, as well as, a refined quantification of seasonal variation. Ammonia and nitrous oxide emission levels were also evaluated for use as predictors of daily wet-fall concentration. Improvements in model accuracy for the expanded study period were achieved. The revised model was implemented to provide direct estimates of daily wet-fall concentration and wet deposition to the land and river modeling segments of the CBW Modeling Program, as well as, for the geographic region surrounding the CBW.

15. SUBJECT TERMS

wet-fall concentration, wet deposition, ammonium concentration, nitrate concentration, ammonium deposition, nitrate deposition, daily concentration model, Chesapeake Bay Watershed

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON James A. Lynch
a. REPORT	b. ABSTRACT	c. THIS PAGE	none	20	
none	none	none			19b. TELEPHONE NUMBER (Include area code) 814-238-0811

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Improved Daily Nitrate and Ammonium Concentration Models for the Chesapeake Bay Watershed

FINAL REPORT

Prepared By:

James A. Lynch, Ph.D., Professor of Forest Hydrology, Consultant,
State College, Pennsylvania

Jeffrey W. Grimm, Cyclimetric Environmental Consulting, Consultant,
Pennsylvania Furnace, Pennsylvania

July 28, 2003

Introduction

The major determinants of wet deposition are the volume of precipitation that falls at a given point and the concentrations of dissolved substances in precipitation at that point. Unlike precipitation volumes, much less is known about the spatial and temporal variations in the concentrations of dissolved substances in precipitation other than what can be discerned from point estimates from routine monitoring programs, such as the National Atmospheric Deposition Program (NADP). This is especially true with regards to daily ammonium and nitrate concentrations. Although it is generally recognized that the concentration of a dissolved substance in precipitation is a function of not only the volume of precipitation, but also local and regional land cover and emission sources, the actual role each plays in determining the concentration at a given location is unknown. Consequently, efforts to define spatial patterns of ionic concentrations in precipitation over a region are generally limited to simple statistical relationships based on observed point estimates within the region and peripheral sites. One such statistical relationship was developed by Valigura et al. (1996) for the Chesapeake Bay Watershed (CBW).

The purpose of the modeling effort described here is to update and improve the accuracy of daily ammonium and nitrate wet concentration models used to provide deposition estimates for the Phase 5 Chesapeake Bay Watershed Modeling Program. The existing daily concentration models described in Linker et al, (1999) and Valigura, et al (1996) were developed from precipitation chemistry and volume data collected at 15 NADP/NTN monitoring stations located in and around the CBW modeling region from 1984 through 1992. This modeling effort incorporated information on sample precipitation volume, month of year, and latitude in a linear regression model of log-transformed wet-fall ammonium and nitrate concentrations. This report details the development of a revised regression model derived from data from the same NADP/NTN monitoring stations from 1984 through 2001 and incorporating additional information describing spatial location, preceding precipitation event history, seasonality, long-term trend, and land use.

Methods and Model Development

The National Atmospheric Deposition Program (NADP) and the National Trends Network (NTN) have been in operation since 1978 and provide chemical analyses for weekly precipitation samples collected at over 220 monitoring sites across the United States in compliance with standardized sample collection and analytical protocols [NADP, 2002; Bigelow and Dossett, 1988; Peden et al, 1979]. Daily precipitation volume records are also collected at each NADP/NTN monitoring site. Twenty-seven of the NADP/NTN sites are located in or adjacent to the CBW modeling region. Quality-controlled weekly measurements of wet-fall ammonium and nitrate concentrations and the corresponding daily precipitation volumes at these NADP/NTN sites constituted the precipitation data set used for model development. Concentrations and precipitation volumes were log-transformed for this analysis. Because this modeling effort involves the development of daily concentration models of inorganic nitrogen compounds only those weekly precipitation chemistry samples that were comprised of a single precipitation event

2

were used for model development. The following measures of precipitation event history were calculated for each precipitation chemistry sample from the daily precipitation records for each NADP/NTN station:

1) The number of days since the preceding precipitation event;
2) the volume of precipitation occurring in the preceding 3, 5, 7, 10, and 14-day periods; and
3) the number of days having precipitation during the preceding 7 and 14-day periods.

Seasonality is represented in the model by dividing each calendar year into six distinct bi-monthly periods. The first bi-monthly period corresponds to January and February and the sixth to November and December. The six seasonal time periods are represented in the linear regression model by an array of five binary indicator variables. Spatial variation in concentration patterns was addressed in predictor selection by including first- and second-degree polynomial terms of latitude and longitude in the set of potential predictors.

In an effort to enhance the accuracy of modeled estimates of daily ammonium and nitrate concentrations additional data describing local land use and ammonia and nitrous oxide emissions were incorporated into the model development process. The 1992 National Land Cover Data (NLCD) grids provide a 30-meter resolution classification derived from LANDSAT thematic mapper imagery that encompasses the CBW modeling region (Vogelmann et al, 1998). The 1992 NLCD was used to calculate proportional representation of several land use categories within the proximities of 0.8, 1.6, 3.2, 8.0, and 16.1 km of each NADP/NTN site for evaluation as potential predictors of daily ammonium and nitrate wet-fall concentrations. The candidate land use categories were open water (code 11), forested (codes 41 through 43), residential (codes 21 and 22), industrial/transportation (code 23), croplands (codes 81 through 84), and vegetated wetlands (codes 91 and 92).

Local emission levels of ammonia and nitrous oxides were also considered as potential predictors of wet-fall daily ammonium and nitrate concentrations. Emissions data were obtained from the United States Environmental Protection Agency's National Emission Trends (NET) database (http://www.epa.gov/air/data/netdb.html). The NET database yields emissions totals for individual counties for each year from 1985 through 1999. For model development, NET annual emission totals were standardized by county area. The area-standardized emissions rates for both the county containing each NADP/NTN monitoring site and for the nearest three counties were used as candidate predictors for the daily concentration models. The nearest counties were determined by the distance from the county centroid to the monitoring site location. Emissions measurements were matched to precipitation chemistry samples by year.

Selection of final model effects from among the set of candidate predictors was conducted using stepwise linear least squares regression with forward selection and backward elimination of terms evaluated at each step based on a significance level of 0.10. The first step of the stepwise regression selection procedure for each ion began with precipitation and seasonality included as predictors. These effects were shown to be significant predictors of both daily ammonium and nitrate wet-fall concentrations by the preceding model development (Valigura et al, 1996). Hierarchy of predictor effects in the regression models was maintained without regard to the

statistical significance of individual component effects. Therefore, the predictors involved in significant compound (interaction) or polynomial effects were retained in the models. The form of the regression model used in our analysis is:

$$log10(c) = b_0 + b_1 log10(ppt) + \Sigma b_{2s} season + b_3 v_3 + \ldots + b_n v_n + e$$

where,

c	= daily wet-fall ionic concentration (mg/L)
b_0	= intercept
ppt	= daily precipitation volume (inches)
b_1	= coefficient for precipitation term
$season$	= vector of 5 binary indicator variables encoding the 6 bi-monthly seasons
b_{2s}	= vector of 5 coefficients for season terms
$v_3 \ldots v_n$	= additional predictors selected through stepwise regression
$b_3 \ldots b_n$	= coefficients corresponding to $v_3 \ldots v_n$
e	= residual error

Estimates of daily ionic deposition were calculated as the product of estimated concentration and daily precipitation volume:

$$d = 0.254 * c * ppt$$

where,

d	= estimated daily ionic wet deposition (kg/ha)
c	= estimated daily ionic wet-fall concentration (mg/L)
ppt	= daily precipitation volume (inches)

Estimates of daily ionic wet deposition rates (kg/ha/day) to the land modeling segments employed by the Phase 5 Watershed Modeling Program for the CBW were calculated by estimating depositions at the cell centers of a uniform 1.09-km grid overlaying the CBW modeling region and then averaging the deposition estimates for grid cell centers lying within each polygon. The product of the polygon deposition rate by the polygon area yields the total daily ionic mass deposition for the polygon.

Results and Interpretation

The models of daily ionic wet-fall concentrations of ammonium and nitrate produced by stepwise regression analyses are detailed in Tables 1 and 2. Precipitation volume was the strongest predictor of both ammonium and nitrate concentrations. Concentrations were inversely related to precipitation volume, although the dilution effect remained nonlinear after logarithmic transformation of both concentrations and volumes (Figures 1 and 2).

4

Table 1. Linear regression model of log-transformed ammonium ion concentration for daily precipitation samples collected within the Chesapeake Bay Watershed modeling region during 1984 through 2001 ($n=3992$, $r^2=0.3148$).

Parameter	Partial Mean Square	F-Value	Significance	Coefficient
Intercept				-1.309916711
Log10(precip)	2.8800	8.29	<0.0001	-7.845308913
Log10(precip^2)	5.5240	35.09	<0.0001	0.646417263
Log10(precip) during preceding 7 days	0.9948	6.32	0.0120	-0.087667650
Number of days since previous precip. event	1.6853	10.70	0.0011	0.045256130
Season (bi-month)	1.3702	8.70	<0.0001	
January-February				0.016137078
March-April				0.185788184
May-June				0.132659903
July-August				0.182198714
September-October				0.155588260
November-December				0.000000000
Log10(precip) X Season	3.6334	23.08	<0.0001	
January-February				0.146259314
March-April				0.472258721
May-June				1.230076364
July-August				0.820622687
September-October				-0.003393801
November-December				0.000000000
Latitude (degrees)	4.1053	26.08	<0.0001	0.191256875
Longitude (degrees)	0.0151	0.10	0.7566	-0.019981068
Log10(precip) X longitude	1.3046	8.29	0.0040	-0.634962386
Long-term trend (year)	5.0743	32.23	<0.0001	0.006641725
Proportion of land within 5-miles covered by forest	6.1682	39.18	<0.0001	-0.357539328
Proportion of land within 0.5-miles covered by forest	0.5796	3.68	0.0551	0.091676853
Proportion of land within 5-miles devoted to industry and transportation	5.3793	34.17	<0.0001	2.444376086

Table 2. Linear regression model of log-transformed nitrate ion concentration for daily precipitation samples collected within the Chesapeake Bay watershed modeling region during 1984 through 2001 ($n=3992, r^2=0.4940$).

| Parameter	Partial Mean Square	F-Value	Significance	Coefficient
Intercept				-14.25901207
Log10(precip)	2.3592	35.55	<0.0001	-10.94975238
Log10(precip^2)	7.4454	112.19	<0.0001	0.75512533
Precip. volume during preceding 7 days (log10)	0.5432	8.18	0.0042	-0.06484770
Number of days since previous precip. event	3.6334	54.75	<0.0001	0.06652244
Season (bi-month)	0.6223	9.38	<0.0001	
January-February				0.00590539
March-April				0.06037087
May-June				0.05062807
July-August				0.14081422
September-October				0.03125004
November-December				0.00000000
Log10(precip) X season	1.5416	23.23	<0.00001	
January-February				0.25861568
March-April				0.50002417
May-June				0.84222455
July-August				0.68102081
September-October				0.16203385
November-December				0.00000000
Latitude (degrees)	0.8457	12.74	0.0004	5.26018889
Longitude (degrees)	0.3305	4.98	0.0257	-1.17334607
Latitude x Longitude	0.4405	6.64	0.0100	0.33919130
Latitude^2	0.5994	9.03	0.0027	-0.29794998
Log10(precip) X Longitude	1.5550	23.43	<0.0001	-0.85397658
Log10(precip) X Latitude	0.3354	5.05	0.0246	0.32250810
Long-term trend (year)	1.8614	28.05	<0.0001	-0.00404099
Proportion of land within 5-miles covered forest	3.3117	49.90	<0.0001	-0.29053387
Proportion of land within 0.5-miles covered by forest	1.9190	28.92	<0.0001	0.16957760
Proportion of land within 5-miles covered by water	1.2483	18.81	<0.0001	-0.37649968
Proportion of land within 0.5-miles covered by water	0.5822	8.77	0.0031	0.23019904
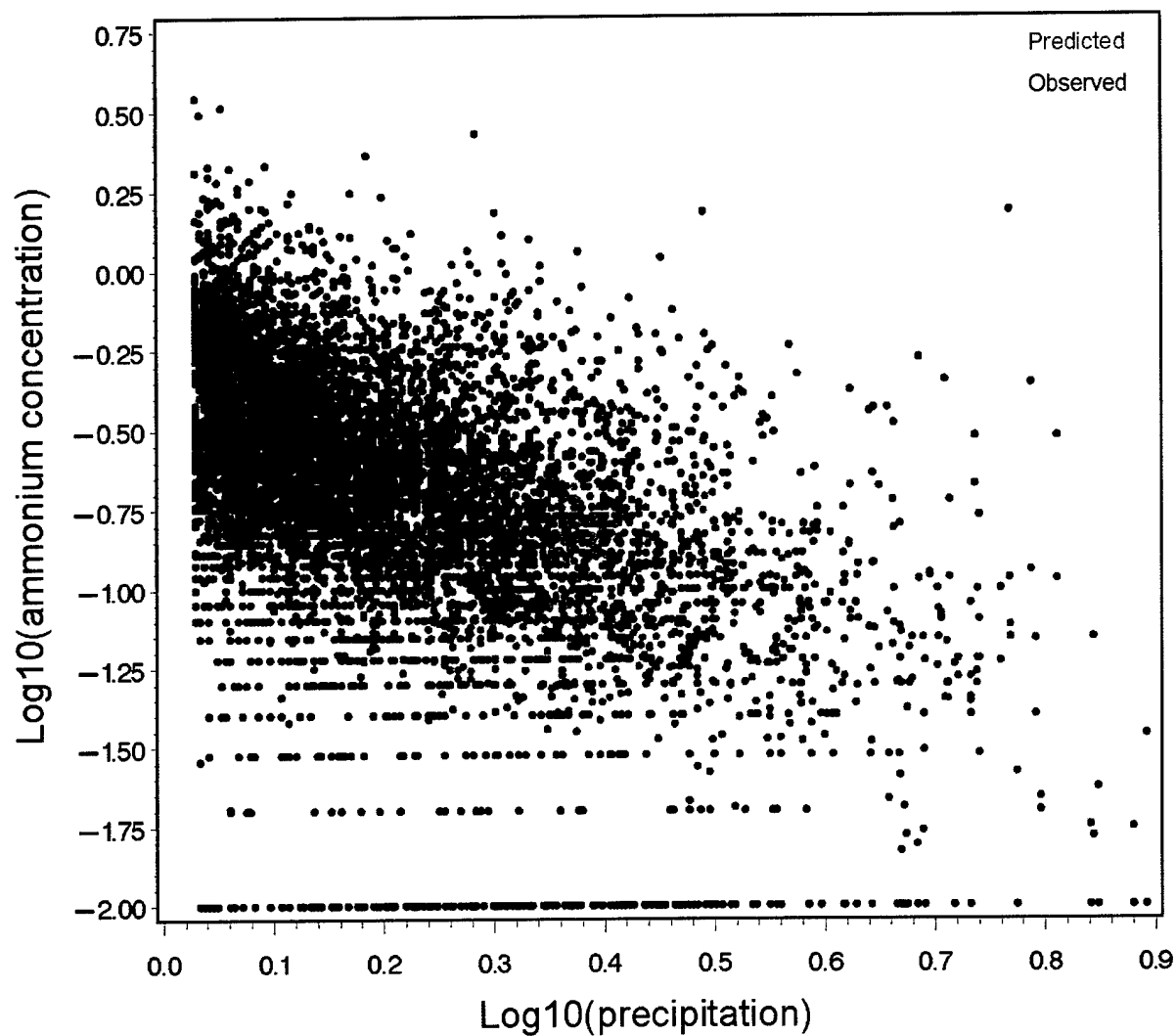
Figure 1. Dilution relationship between predicted and observed single-event ammonium
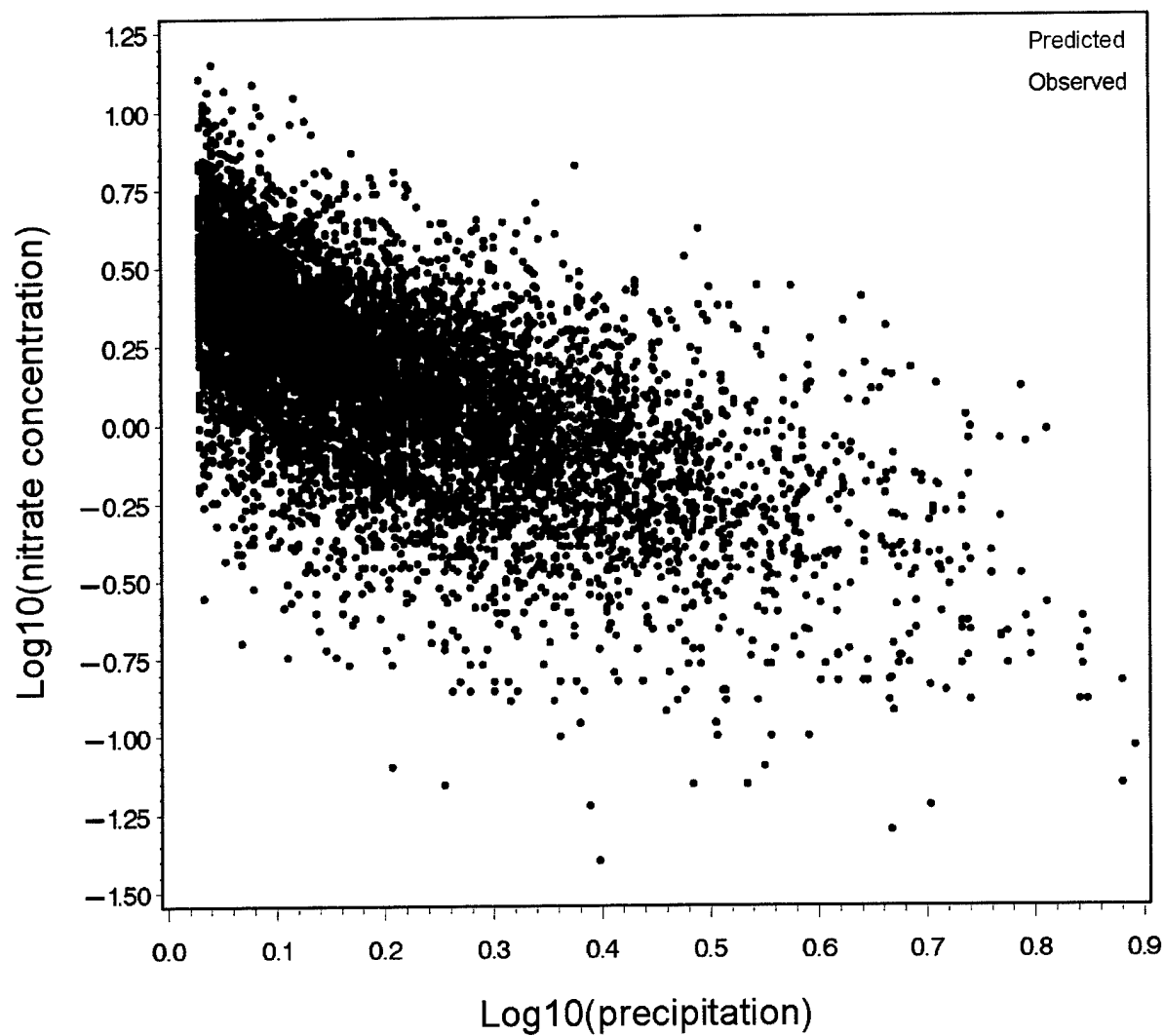wet-fall concentrations at 28 NADP/NTN sites in the CBW region during 1984-
2001.

Figure 2. Dilution relationship between predicted and observed single-event nitrate wet-fall concentrations at 28 NADP/NTN sites in the CBW region during 1984-2001.

The dilution effect exhibited both seasonal and spatial variability. Dilution rates were strongest during the fall and winter months and weakest during the late spring and early summer months for both ammonium and nitrate. Dilution rates also tended to increase toward the eastern portions of the study area, and for nitrate, also tended to be weaker in the northern portion of the study area. Concentrations of both inorganic nitrogen compounds were generally higher during the spring and summer months. A latitudinal gradient was apparent in the concentrations for both species. Log-transformed concentrations of ammonium tended to increase linearly with latitude. Nitrate concentrations also tended to be higher toward the north, but the tendency was non-linear and confounded with longitudinal gradients in concentration and dilution rate. Significant long-term trends in concentration were observed for both nitrogen compounds. Wet-fall ammonium concentrations tended to increase during the 1984 to 2001 period; whereas nitrate concentrations in precipitation tended to decline during the same period.

Precipitation event history was a significant factor in wet-fall concentrations of both ammonium and nitrate. Concentrations of both species were directly related to the number of days since the preceding precipitation event. This effect was more pronounced for nitrate than ammonium. The volume of precipitation falling during the preceding seven days exhibited a significant, but moderate, inverse relationship to wet-fall concentrations.

Both land use composition and emissions levels showed significant relationships to the wet-fall concentrations of ammonium and nitrate. However, the elements of these two categories of predictors tended to displace each other in the stepwise regression selection process. Inclusion of a subset of the land use composition variables in the concentration models yielded slightly higher model r^2 values (0.315 vs. 0.296 for ammonium and 0.494 vs. 0.490 for nitrate) and the contributions of emission levels in the models, in addition to land use effects, were not significant at the 0.1-level. As expected, wet-fall concentrations of ammonium were directly related to area-standardized emissions of ammonia ($p < 0.0001$), and nitrate concentrations were directly related to emissions of nitrous oxides ($p < 0.0001$). Ammonium concentrations were better predicted by emissions rates for the individual county containing the monitoring site than by the mean levels for the nearest three counties. Conversely, nitrate concentrations showed stronger relationships to mean emission rates for the nearest three counties than for the immediate county. The observed relationships of wet-fall concentrations to land use composition were more complex and less intuitive than for emissions rates. Concentrations of both ammonium and nitrate were strongly, inversely related to the extent of forest cover within 8 km of a monitoring site; however, a weaker direct relationship exists with the amount for forest cover within 0.8 km. Concentration levels of ammonium were also directly associated with the extent of industrial and transportation land uses within 8 km. The stepwise predictor selection process identified the relative extent of open water in the surrounding 8- and 0.8-km proximities as a significant predictor of nitrate concentrations. The functional relationship between nitrate concentration and prevalence of surface water is not certain, but may reflect influences of coastal air masses on precipitation chemistry. No inflation of standard errors of regression coefficients was observed with the successive addition of land cover predictors to the models for either inorganic nitrogen compound. Thus, there was no evidence of multi-colinearity of predictor variables. The decision to incorporate land use composition rather than emissions levels into the final daily ammonium and nitrate concentration models was based on the slightly better model performance and on the consistent availability of land use composition data for use in the model.

At the time of this report (July, 2003), ammonia and nitrous oxides emissions estimates were only available from 1985 through 1999, and thus, were not applicable to the entire duration of the 1984 through 2001-study period.

An earlier daily ammonium wet-fall concentration model was been developed using weekly precipitation chemistry samples in which precipitation occurred during the last day of the sampling period (Valigura et al, 1996). This restriction was imposed because of the decrease of ammonium concentrations in samples over time. We included other single-event weekly samples in our final model development because precipitation event history was indicated to be a significant factor in rainfall concentration levels. Restricting sample selection to those with rainfall only in the final day of the sample period would have precluded observations with rainfall occurring during the preceding six days. Studies of ammonium and nitrate concentrations in weekly versus daily sampling protocols have indicated that both inorganic nitrogen species are higher (generally 4 to 10 percent) for daily sampling protocols than for weekly protocols (de Pena et al., 1985; Lamb and Comrie, 1993; Sirois et al., 1985; Butler and Likens, 1995; Rothert et al., 2000; Gilliland et al., 2002). This is especially true for ammonium concentrations. Furthermore, NADP/NTN precipitation samples are transported by over-land commercial carriers from field sites to a centralized analytical laboratory located in Champaign, Illinois. The period of time samples are in transit ranges from one to seven days, sometimes longer. Consequently, a decrease in inorganic nitrogen concentrations, especially ammonium, occurs for all weekly precipitation chemistry samples regardless of the day that precipitation occurred, including those samples that include precipitation that fall on the last day of the sampling period.

Fitting the regression parameters of the model previously used for estimating daily ammonium and nitrate concentrations (Valigura et al, 1996) to the data for 1984 through 2001 shows that the functional relationships between the predictors and concentrations have remained similar (Table 3). However, the amplitude of the seasonal variation and the dilution rates for both inorganic nitrogen compounds declined when this model was applied to the expanded data set. Also, the predictors of the earlier model did not provide the same degree of fit to the more recent concentration data as they did to the data from 1984 through 1992. This change in model performance may be due, in part, to the long-term trends in wet-fall concentrations from 1982 to 2001. However, the data set used for our analyses contained observations from 28 NADP/NTN sites, as opposed to, observations from only 15 sites from the development of the earlier model. The data set for the current analyses very likely contains more sources of temporal and spatial variability than the data from which the preceding model was developed.

Estimates of mean event wet deposition from our model agree well with the observed depositions at the six AIRMoN sites in operation within the CBW during 1992 through 2001 (Table 4). However, measured individual event concentrations and depositions often varied widely from the estimated values. Valigura et al (1996) noted single event departures of nearly 10-fold when comparing estimates from their model to observations recorded at three MAP3S sites in the CBW. Departures of similar size from our model were also seen in single-event records from the AIRMoN sites as well. In spite of these large, single-event variations, the correlations between observed and estimated event depositions remained high. Applying our daily concentration models to the daily precipitation records from 1984 through 2001 for 28 NADP/NTN precipitation chemistry sites located in or adjacent to the CBW region and summing the

10

deposition estimates into annual totals provides a comparison with the observed annual deposition at those sites (Table 5). These estimation error rates show a modest improvement over the 19 percent mean errors for annual depositions reported by Valigura et al (1996) for 15 NADP/NTN sites in the CBW during 1984 through 1992. The error rates for the present model are based on observations from a longer time period (17 years vs. 8 years), a larger number of monitoring sites, and a set of precipitation chemistry samples that were not restricted to events occurring in the last day of the weekly sampling period.

The revised daily concentration models were applied to grids of estimated daily precipitation from two different sources to calculate grids of estimated ammonium, nitrate, and total inorganic nitrogen wet deposition. The first was from the United State Weather Service, Climate Prediction Center's Daily Precipitation Analyses (http://www.cpc.ncep.noaa.gov/products/ precip/realtime/ us_precip.html). These precipitation grids are produced 0.25-degree resolution for the continental United States and southern Canada by applying a modified Cressman spatial interpolation algorithm to quality-controlled observations from River Forecast Center gauges (3000 to 6000 stations) and the Climate Anomoly Database. Because of the large spatial coverage of the CPC grids, these data were used to estimate depositions across the broad region encompassing the CBW region (Figures 3 through 6). Figures 3 and 4 illustrate the inverse relationship between precipitation volume and wet-fall ammonium and nitrate concentrations, respectively; consequently, these figures also show a general inverse spatial relationship between wet-fall concentration and deposition for an individual precipitation event. Grids of estimated daily deposition were summed to produce grids of annual estimated concentrations. In turn, these annual grids were averaged for the period 1985 through 2001 to produce estimates of mean annual wet deposition (Figures 5 and 6). Figure 5 shows general latitudinal and longitudinal gradients of wet deposition of both ammonium and nitrate. However, the localized influence of land cover on ammonium wet-fall that is incorporated into our model is evident in the more spatially-irregular deposition field for that species.

Higher resolution grid estimates of daily precipitation from a precipitation model developed for the river modeling segments within the Phase 5 CBW modeling region were also integrated into our daily concentration model. This precipitation model was developed by the United States Geological Survey and produces estimates at 5-km resolution for grids that cover only the Phase 5 river modeling segments. At the time of this report (July 2003), precipitation estimates were only available for 1984 through 1999. Although the summary periods are not identical, the grid of estimated mean annual deposition based on inputs from the U.S.G.S. precipitation model (Figure 7) shows very similar overall patterns to that based on the CPC's precipitation estimates (Figure 6). However, modeled depositions based on the U.S.G.S. model are greater in some areas of high topographic relief, such as the mountains of central Pennsylvania and western Maryland. This departure from estimates based on the CPC precipitation data is expected because the CPC interpolation algorithm does not directly adjust estimates for orographic effects and high elevation locations are not well represented among the river forecasting gauges employed by the CPC analyses. Topography is known to have a strong influence on local precipitation volume (Barros and Lettenmaier, 1993, 1994); and, consequently, also on wet deposition rates.

11

Table 3. Comparison of regression parameters from the previous CBW daily wet-fall concentration models with those estimated from more recent data. The original parameter estimates were derived from NADP/NTN data from 1984 through 1992 (Valigura et al, 1996). The revised estimates are calculated from NADP/NTN data from 1984 through 2001. Only samples composed of single events occurring in the last day of the weekly sample period were used for estimation of parameters.

Parameter	Parameters Of Original Model	Updated Model Parameters
Number of samples	265	569
--------- $\log_e$(ammonium ion concentration) ----------		
Intercept	-1.2260	-1.16219
Log_e(precip)	-0.3549	-0.23634
Month	0.3966	0.13398
Month^2	-0.0337	-0.01219
Model r^2	0.31	0.2163
--------- $\log_e$(nitrate ion concentration) ----------		
Intercept	-1.289	-1.66975
Log_e(precip)	-0.3852	-0.25591
Month^2	-0.0037	-0.00154
Latitude	0.0744	0.04177
Model r^2	0.41	0.3434

Table 4. Comparison of mean estimated daily ammonium and nitrate wet-fall depositions with observed event wet depositions at 6 AirMon sites located within the CBW region during 1982 through 2001.

Site	Mean Observed Deposition	Mean Estimated Deposition	Mean Error	Mean Absolute Error	Correlation between obs. and est. dep.
		------------ Ammonium (kg/ha) ------------			
DE02	0.03303	0.03571	0.00268	0.01964	0.5431
DE99	0.04266	0.03502	-0.00765	0.02217	0.5702
MD15	0.02892	0.03163	0.00270	0.01771	0.5906
NY67	0.02615	0.02232	-0.00384	0.01517	0.6560
PA15	0.03176	0.02781	-0.00395	0.01674	0.7252
WV99	0.02070	0.02080	0.00009	0.01222	0.6933
Overall	0.02976	0.02809	-0.00167	0.01784	0.6078
		------------ Nitrate (kg/ha) ------------			
DE02	0.16215	0.13746	-0.02468	0.10054	0.5043
DE99	0.12361	0.13680	0.01320	0.09103	0.5216
MD15	0.14692	0.14233	-0.00459	0.08684	0.5638
NY67	0.14574	0.15336	0.00763	0.07334	0.6447
PA15	0.17676	0.17692	0.00016	0.07945	0.6542
WV99	0.09180	0.10323	0.01143	0.04350	0.7237
Overall	0.15443	0.15471	0.00027	0.08166	0.5879

Table 5. Comparison of estimated annual wet depositions of ammonium, nitrate, and total inorganic nitrogen calculated for the daily wet-fall deposition model with annual deposition observed at 28 NADP/NTN monitoring sites in or adjacent to the CBW region during 1984 through 2001. All depositions are expressed as kg/ha.

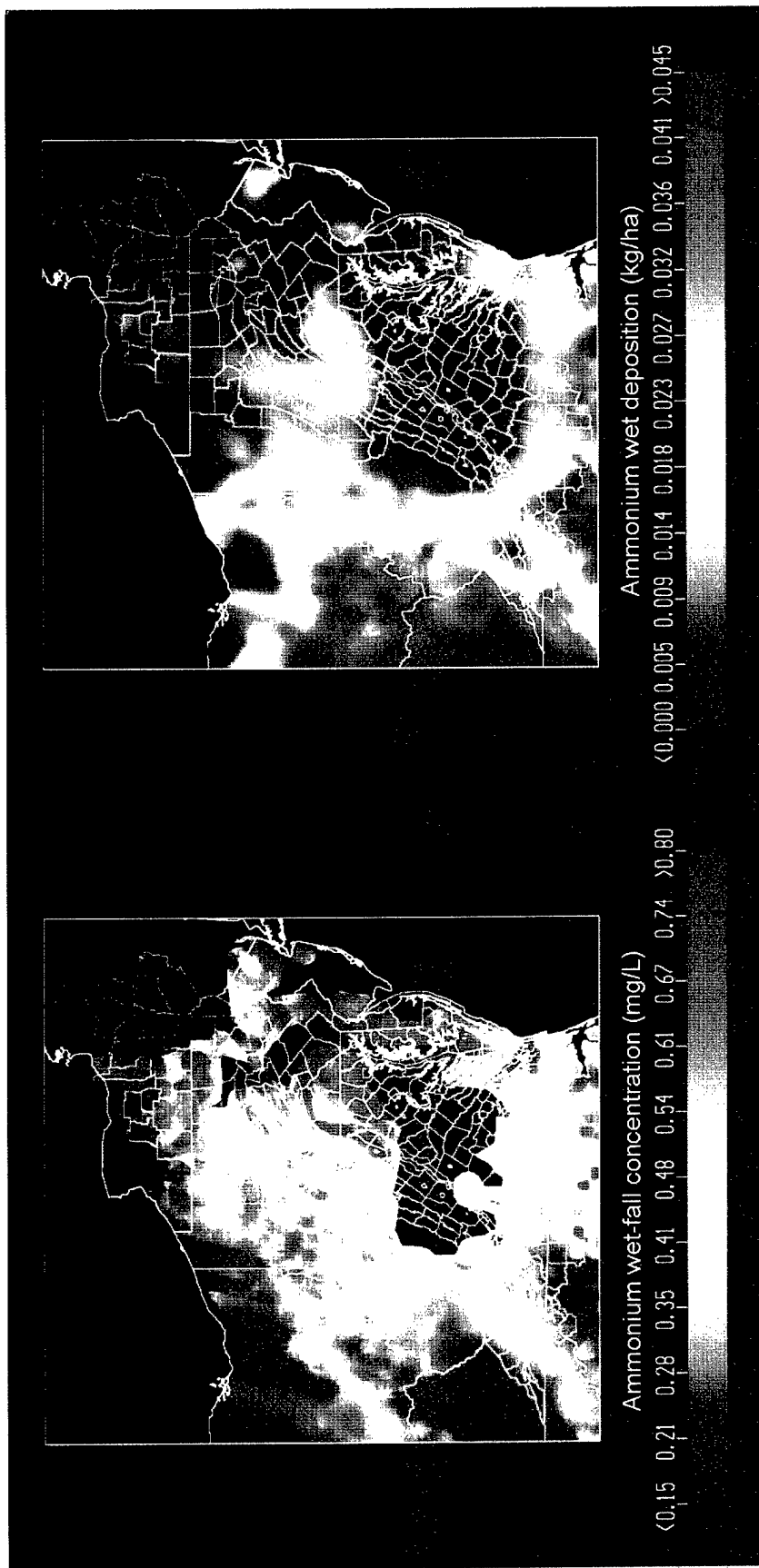| Parameter	Total Inorganic Nitrogen Deposition	Ammonium Deposition	Nitrate Deposition
Observed Mean	5.471	2.636	15.14
Estimated Mean	5.100	2.481	14.30
Mean Error	-0.371	-0.156	-0.85
Mean Absolute Error	0.810	0.496	2.36
Mean Percent Error	16.7	19.0	15.5

13

Figure 3. Estimated daily ammonium wet-fall concentration and wet deposition across the Chesapeake Bay Watershed region and portions of adjacent states on 1 May 1998. These estimates were produced by applying the daily ammonium concentration model to grids of estimated daily precipitation from the National Weather Service Climate Prediction Center's U.S. Daily Precipitation Analyses (http://www.cpc.ncep.noaa.gov/products/precip/realtime/us_precip.html). Land areas not receiving precipitation on 1 May 1998 appear as black in these images.

14
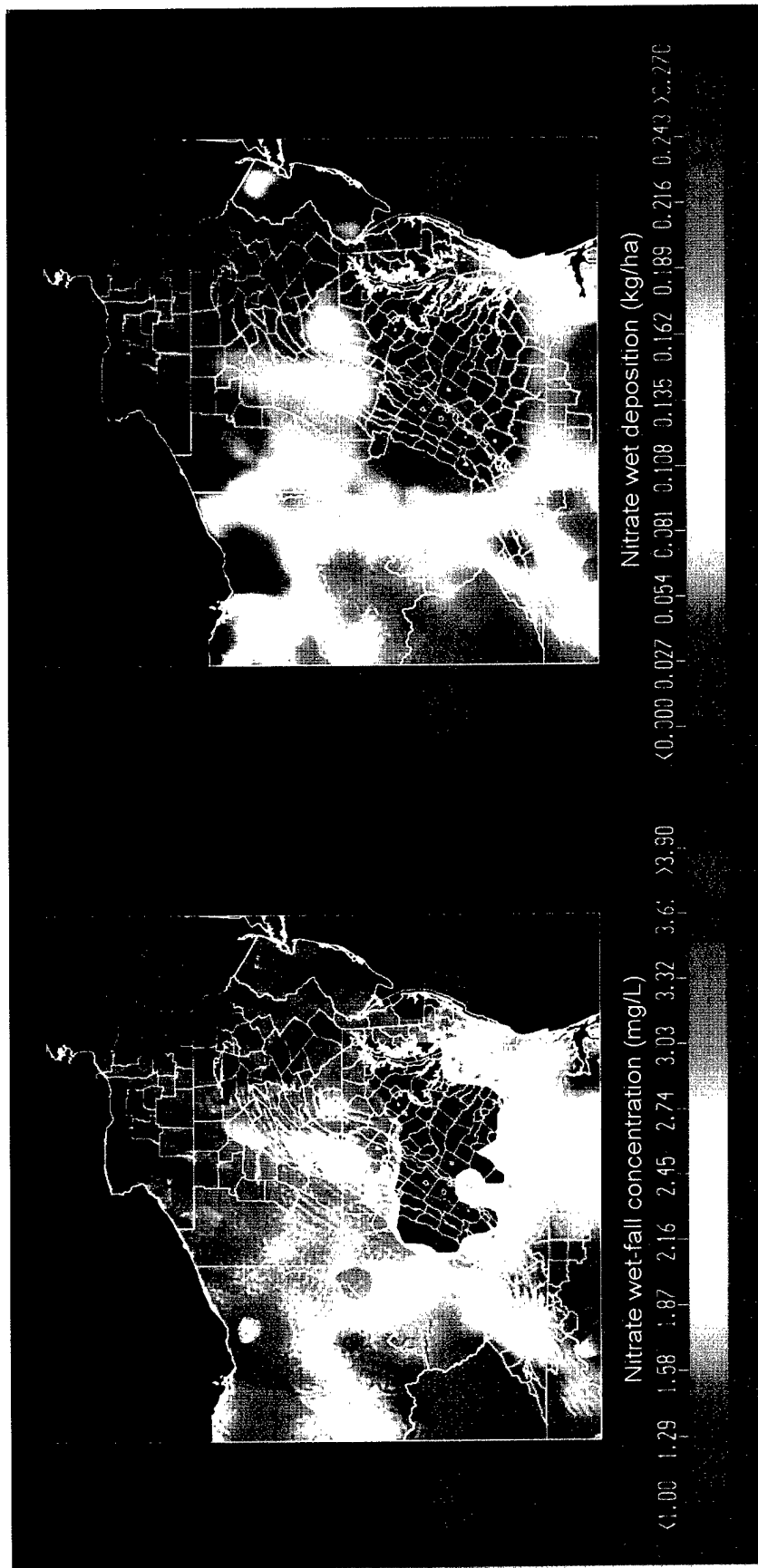
Figure 4. Estimated daily nitrate wet-fall concentration and wet deposition across the Chesapeake Bay Watershed region and portions of adjacent states on 1 May 1998. These estimates were produced by applying the daily nitrate concentration model to grids of estimated daily precipitation from the National Weather Service Climate Prediction Center's U.S. Daily Precipitation Analyses (http://www.cpc.ncep.noaa.gov/products/precip/realtime/us_precip.html). Land areas not receiving precipitation on 1 May 1998 appear as black in these images.
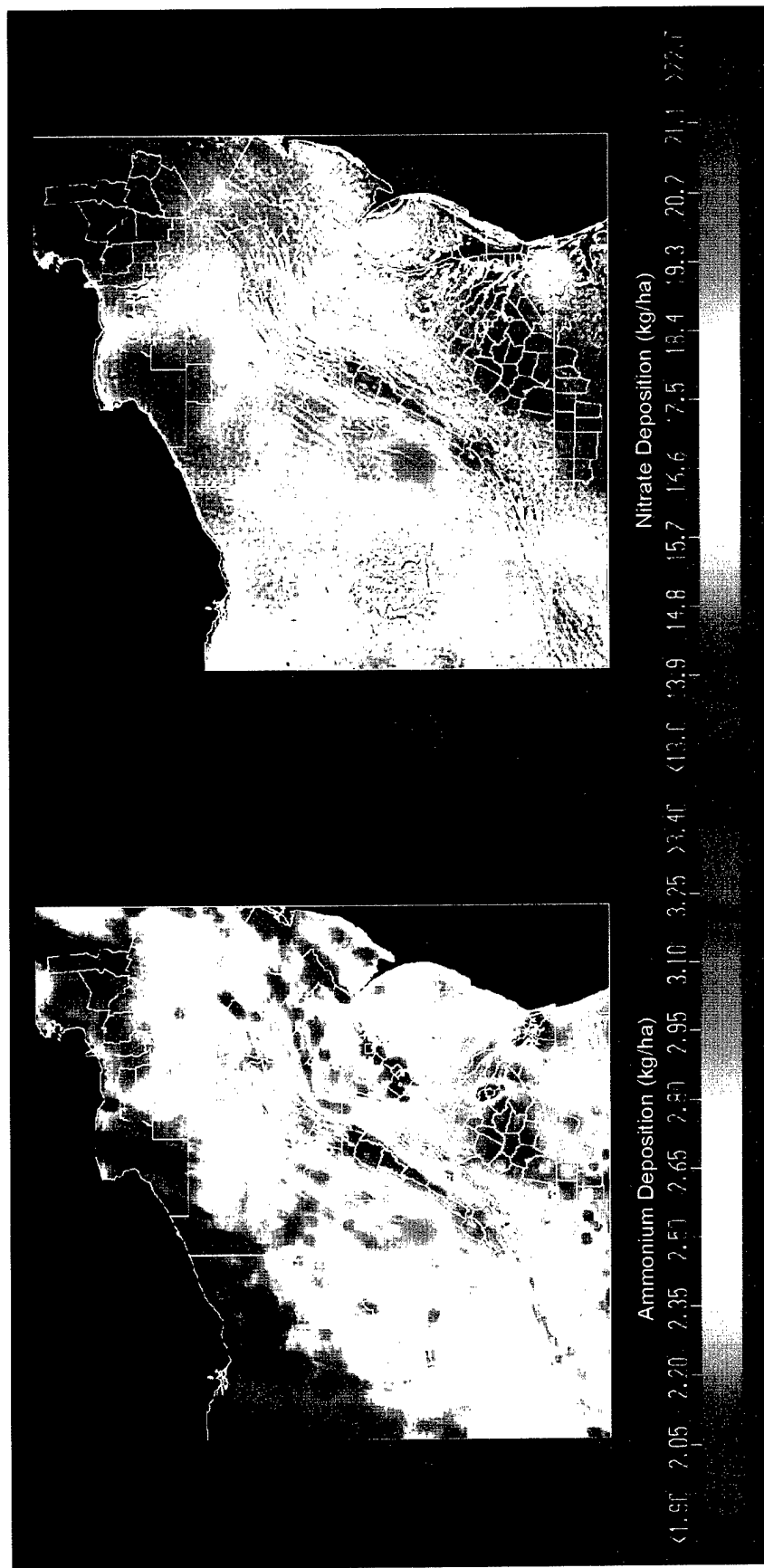
15

Figure 5.   Estimated mean annual wet deposition of ammonium and nitrate across the Chesapeake Bay Watershed region and portions of adjacent states during 1985 through 2001. These estimates were produced by applying the daily ammonium and nitrate concentration models to grids of estimated daily precipitation from the National Weather Service Climate Prediction Center's U.S. Daily Precipitation Analyses (http://www.cpc.ncep.noaa.gov/products/precip/realtime/us_precip.html).

Nitrogen Deposition (kg/ha)

‹4.75   4.60   4.95   5.30   5.65   6.00   6.35   6.70   7.05   7.40   ›7.75
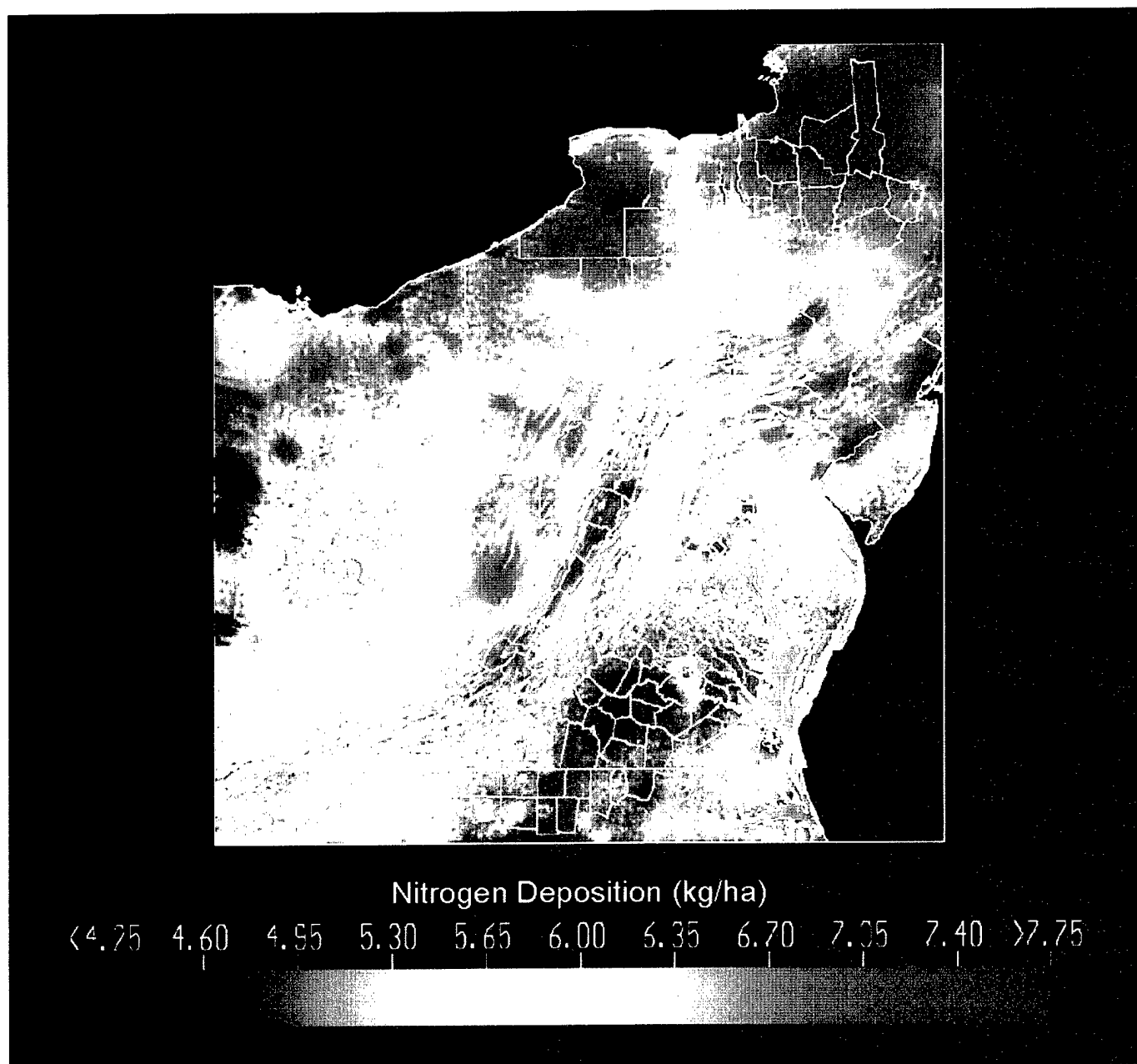
Figure 6. Estimated mean annual wet deposition of total inorganic nitrogen across the Chesapeake Bay Watershed region and portions of adjacent states during 1985 through 2001. These estimates were produced by applying the daily ammonium and nitrate concentration models to gridded estimates of daily precipitation from the National Weather Service Climate Prediction Center's U.S. Daily Precipitation Analyses (http://www.cpc.ncep.noaa.gov/products/precip/realtime/us_precip.html).
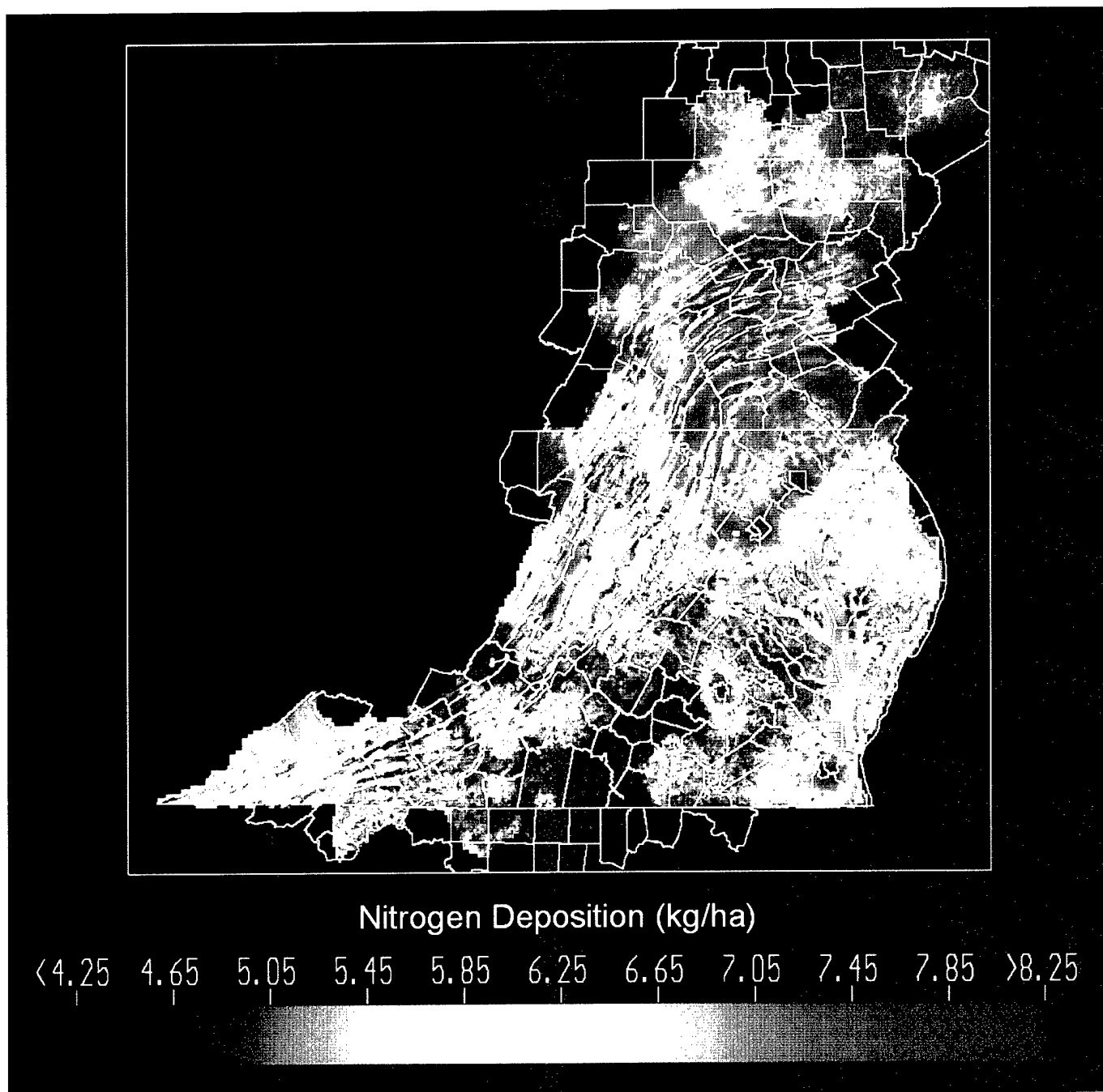
Figure 7. Estimated mean annual wet deposition of total inorganic nitrogen across the Chesapeake Bay Watershed river modeling segments during 1985 through 1999. These estimates were produced by applying the daily ammonium and nitrate concentration models to estimates of daily precipitation from a high resolution hourly precipitation model developed by the United States Geological Survey for river modeling segments in the Chesapeake Bay Watershed study area.

Literature Cited

Barros, A.P. and D.P. Lettenmaier. 1994. Dynamic modeling of orographically-induced precipitation. *Reviews of Geophysics*, **32**(3):265-284.

Barros, A.P. and D.P. Lettenmaier. 1993. Dynamic modeling of the spatial distribution of precipitation in remote mountainous areas. Mon. Weather Rev., **121**:1195-1241.

Bigelow, D. S. and S. R. Dossett. 1988. Instruction Manual for NADP/NTN Site Operation. National Atmospheric Deposition Program, NREL, Colorado State University, Fort Collins, CO.

Butler, T.J. and G.E. Likens 1998. Weekly and daily precipitation chemistry network comparisons in the Eastern US: NADP/NTN vs MAP3S/Airmon. *Atmospheric Environment*, **32**: 3749-3765.

de Pena, M. E., R.C. Walker, L. Lebowitz, and J.G. Micka. 1985. Wet deposition monitoring effect of sampling period. *Atmospheric Environment*, **19**:151-156.

Gilliland, A.B., T.J. Butler, and G. E. Likens. 2002. Monthly and annual bias in weekly (NADP/NTN) versus daily (AIRMoN) precipitation chemistry data in the Eastern USA. *Atmospheric Environment*, **36**:5197-5206.

Lamb, D. and L. Comrie. 1993. Comparability and precision of MAP3S and NADP/NTN precipitation chemistry data at and acidic site in Eastern North America. *Atmospheric Environment*, **27A**: 1993-2008.

Linker, L.C., G.W. Shenk, R.L. Dennis, and J.L. Sweeney. 1999. Cross-Media Models for the Chesapeake Bay Watershed and Airshed November, 1999. Chesapeake Bay Program Office, Annapolis, MD. http://www.chesapeakebay.net/modsc.htm.

National Atmospheric Deposition Program/National Trends Network. 2002. NADP/NTN Annual Data Summary. Precipitation Chemistry in the United States. 2001. The Illinois State Water Survey, Champaign, IL. http://nadp.sws.uiuc.edu/

Peden, M.E., L.M. Skowron, and F.M. McGork. 1979. Precipitation sample handling, analysis, and storage procedures. Research Report No. 4. Illinois State Water Survey, Champaign, IL.

Robert, J., A. Sirois, R. Vet, and D. Lamb. 2000. A comparison of the precipitation chemistry measurements obtained by the CAPMon and NADP/NTN networks. *Environmental Monitoring and Assessment*, **62**:273-303.

Sirois, A., D.L. Sisterson, B.E. Wurfel, and M.M. Lesht. 1985. Chemical differences between event and weekly precipitation samples in Northeastern Illinois. *Atmospheric Environment*, **19**:1453-1469.

Valigura, R., Luke, W., Artz, R., and Hicks, B. (1996). "Atmospheric nutrient input to coastal areas - reducing the uncertainties." *NOAA Coastal Ocean Program Decision Analysis Series No. 9*, Silver Spring, MD.

Vogelmann, J.E., T. Sohl, S.M. Howard, and D.M. Shaw. 1998. Regional land cover characterization using Landsat Thematic Mapper data and ancillary data sources. *Environmental Monitoring and Assessment*, **51**:415-428.